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Spectroscopic studies of excited Tm^{3+} ions in CaF_2 crystals

T. Szczurek* and M. Schlesinger
Department of Physics, University of Windsor, Windsor, Ontario, Canada N9B 3P4

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Vacuum-ultraviolet absorption of CaF_2:Tm^{3+} crystals illuminated with infrared radiation were investigated. Transitions involving absorption of two successive photons were observed. Lifetime in the $^3H_4$ multiplet of Tm^{3+} ions while in clusters was found to be 140±10 ms at liquid-nitrogen temperature.

INTRODUCTION

Optical transitions between electronic states of the triply ionized lanthanides are predominantly of electric dipole nature. Those transitions are parity forbidden within the same electronic configuration. If the ion is in a solid at a site which is noncentrosymmetric, odd-order terms in the crystal-field expansion admix states of opposite parity into the configuration and electric dipole transitions become allowed. The oscillator strengths of those imposed electric dipole transitions are host dependent and as a rule remain quite weak (of the order of 10^{-6}). Electric dipole transitions between $4f$ and $5d$ configurations are parity allowed and have typically oscillator strengths of 10^{-2}.

We have in the past investigated, systematically, and reviewed recently[1] the $4f \rightarrow 5d$ absorption spectra of the triply ionized rare earth (R^{3+}). Despite the great complexity of the spectra and the experimental difficulty of the transitions occurring in the vacuum-ultraviolet region (VUV), one was able to contribute[2] to the understanding of the electron-phonon interactions in the CaF_2:R^{3+} systems.

In the present work, we study a $4f^{12} \rightarrow 4f^{11}5d$ transition in Tm^{3+} not from the ground but from an excited state of the $4f^{12}$ configuration. It will become evident that under suitable conditions a transition such as this is amenable for observation in the form of optical absorption. The transition involves absorption of two successive photons. The first excites the ion within the $4f$ configuration while the second promotes an electron into the $5d$ shell.

Also, at least as far as local phonon frequency is concerned, it is the final $4f^{11}5d$ state that interacts with the lattice, since it appears independent of the initial $4f^{12}$ level. This is in harmony with previously made[2] suggestions.

EXPERIMENTAL PROCEDURE

Crystals of CaF_2:Tm^{3+} were grown and supplied by Optovac, Inc. Samples of adequate dimensions were prepared by either cleaving or cutting and subsequent polishing.

Figure 1 is a schematic of the experimental setup used in the spectroscopic studies of the optically excited Tm^{3+} ions in CaF_2. The ions were excited using infrared (ir) radiation produced by a 200-W tungsten-halogen lamp with a gold-coated reflector. The ir was chopped with a frequency of 0.5 Hz. The spectral range of the ir extended from about 1.05 μm, the switch-on wavelength of the silicon window (0.25 mm), up to about 3.5 μm, the cutoff wavelength of the quartz envelope of the halogen lamp. The sample ($5 \times 5 \times 10$ mm^3) was mounted in a liquid-nitrogen cryostat in front of the exit slit of a McPherson model No. 225 vacuum monochromator. A Hinteregger hydrogen lamp served as a source of the VUV radiation.

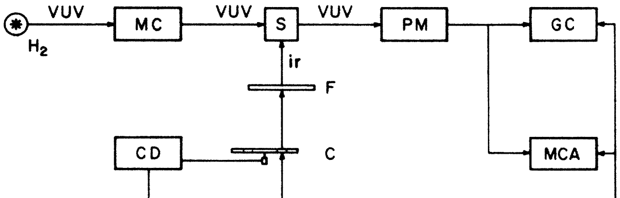

FIG. 1. Schematics of the experimental setup for the absorption spectrum and lifetime measurements of Tm^{3+} ions in excited state. H_2, VUV source; MC, McPherson model No. 225 monochromator; *S*, sample; PM, photomultiplier; GC, gated counters; MCA, multichannel analyzer; *F*, silicon filter; *C*, chopper; *H*, halogen lamp; CD, chopper drive.

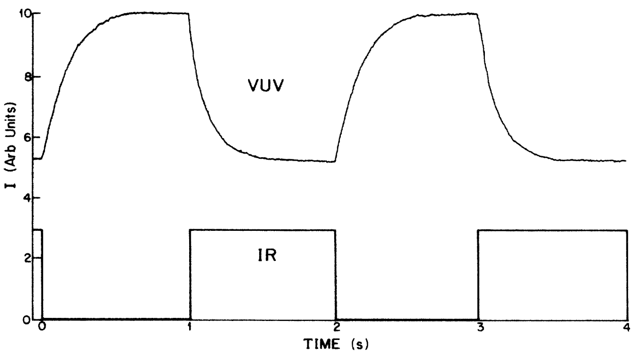

FIG. 2. Time evolution of the VUV transmitted by sample while Tm^{3+} ions are excited by ir as shown.

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A monochromatic VUV beam transmitted by the sample was converted into blue light using sodium salicylate and finally detected by an EMI 9635B photomultiplier followed by electronics operating in a single-photon counting mode. Due to chopping of the ir, modulation of the transmitted VUV was observed as shown in Fig. 2. The lower curve (square wave) represents the chopped ir, while the upper the modulated VUV. The resulting counts were accumulated during many periods using a multichannel analyzer (Nuclear Data model No. 2400) until sufficient signal-to-noise ratio was arrived at. The main source of noise was the slight instability of the VUV lamp.

During the first half of the period, the ir is off and the intensity of the transmitted VUV follows Beer's law

$$\log_{10}(I_\infty/I_t=\epsilon Cl\ ,$$

where I_t and I_∞ are the intensity of the VUV at a given t and $t=\infty$, respectively, l is the thickness of the sample, ϵ is the molar extinction coefficient characterizing a single excited Tm^{3+} ion, and $C=C_0e^{-t/\tau}$ is the concentration of the excited Tm^{3+} ions decaying at the rate of $1/\tau$. The time evolution of the VUV transmitted light by the sample was analyzed using the above relationships, resulting in the determination of the lifetime τ.

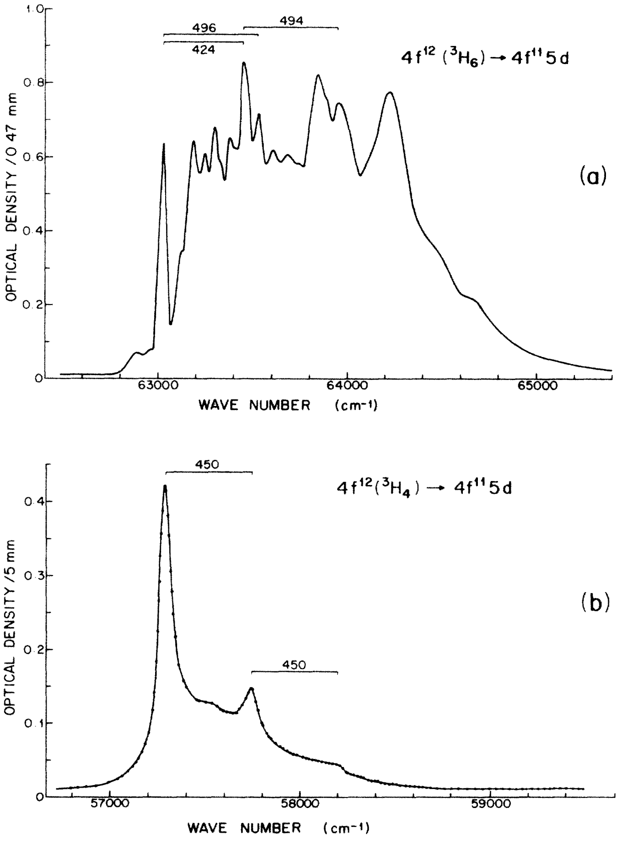

FIG. 3. (a) Vacuum ultraviolet absorption spectrum of a $\mathrm{CaF_2{:}Tm^{3+}}$ crystal taken at liquid-helium temperature. Impurity concentration is 0.05 at. %. Sample thickness is 0.47 mm. Spectral resolution is 4 $\mathrm{cm^{-1}}$. (b) Absorption spectrum of ir excited $\mathrm{CaF_2{:}Tm^{3+}}$ taken at liquid-nitrogen temperature. Impurity concentration is 1 at. %. Sample thickness is 5 mm. Spectral resolution is 8 $\mathrm{cm^{-1}}$.

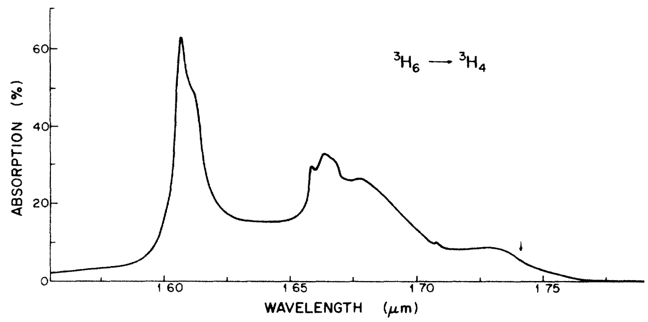

FIG. 4. ir absorption spectrum of the same sample as in Fig. 3(b) taken at liquid-nitrogen temperature.

The VUV spectrum of the excited Tm^{3+} ion was determined as a function of wavelength (point by point) using two photon counters (Ortec model No. 3315) gated synchronously with the chopper. The first counted the VUV photons when ir was on, while the other when ir was off. The transmittance of the sample at a particular wavelength was calculated as a ratio of counts registered by these two counters. In order to increase the accuracy, counts were integrated into 60 chopper periods. The final content of each counter was of the order of 10^7. Thus an accuracy of better than 0.1% was achieved.

The VUV absorption spectra of the Tm^{3+} ion in the ground-state $4f^{12}(^3H_6)$ were recorded using the double-beam spectrophotometer described elsewhere.[3]

The ir absorption spectra were recorded using a Cary 14 spectrophotometer.

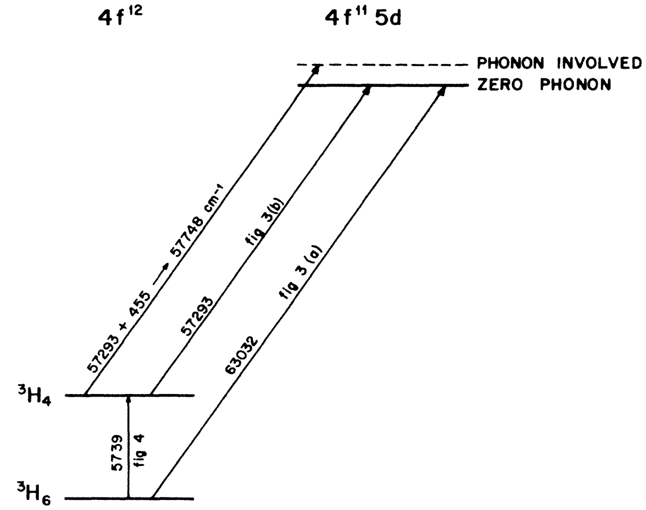

FIG. 5. Energy-level diagram in $\mathrm{CaF_2{:}Tm^{3+}}$ for the absorption features shown in Figs. 3 and 4.

RESULTS

Figure 3(a) represents the VUV absorption spectrum taken at liquid-helium temperature of a $CaF_2:Tm^{3+}$ with impurity concentration (in the melt) of 0.05 at. %. The spectrum is characteristic of lowest-energy $4f^n \rightarrow 4f^{n-1}5d$ transitions in many triply ionized rare earths in the CaF_2 host. (See, for instance, Ref. 1 and references cited therein.) Note the presence of two prominent zero phonon absorption lines separated from each other by ≈ 424 cm^{-1} and their accompanying local phonon lines separated 496 cm^{-1} from their respective parent lines.

Figure 3(b) shows an absorption spectrum of the excited Tm^{3+} ion in the CaF_2 host at the photon energy region of 57 500 cm^{-1}. This spectrum was taken at liquid-nitrogen temperature, and the Tm^{3+} impurity concentration (in the melt) was 1at. %.

Figure 4 represents the near ir absorption spectrum taken at liquid-nitrogen temperature of the crystal corresponding to Fig. 3(b). Figure 5 is a schematic presentation of the energy levels involved in the present study.

DISCUSSION

As in the past,[1] the spectrum presented in Fig. 3(a) is attributed to the lowest $4f^{12}(^3H_6) \rightarrow 4f^{11}5d$ transitions in the Tm^{3+} ion in the CaF_2 host. In spite of the complexity of the component peaks, it is possible to identify at least two zero phonon lines and their accompanying ≈ 495-cm^{-1} phonon side bands. The phonon side band peak near 490 cm^{-1} accompanying $4f^n \rightarrow 4f^{n-1}5d$ transitions of most triply ionized rare-earth elements in the CaF_2 matrix and some of the corresponding peaks in SrF_2 and BaF_2 have been reliably identified[2] as a local mode associated with the rare-earth ion and its nearest-neighbor fluorine ions. In addition, it was found that the phonon frequency is nearly independent of (i) the rare-earth ion and (ii) shifts in the position of the zero phonon line due to different modes of charge compensation.

The spectrum presented in Fig. 3(b) should be identified as the lowest $4f^{12}(^3H_4) \rightarrow 4f^{11}5d$ transition in the Tm^{3+} ion in the CaF_2 host. The transition is accompanied by a phonon side band peak at ~ 450 cm^{-1} away and an additional (rather weak) peak at $2 \times 450 \cong 900$ cm^{-1} from the parent zero phonon line. Previous results[4] have shown that in the case of relatively high impurity concentrations, a tendency of dopant clustering develops. As a result, a change of local mode frequency is detected. The value of ~ 450 cm^{-1} in the present case is in excellent agreement with the values observed in Eu^{3+} and Pr^{3+} clusters.[4]

The identification of the peak at 57 293 cm^{-1} as originating from the excited $4f^{12}(^3H_4)$ level (see Fig. 5) is supported by a careful study of Figs. 3(a) and 4. In Fig. 4 we indicate by an arrow the spectral position of the level from which the transition is assumed to originate. It is observed that (1) the transition originates at 5739 cm^{-1} and as such is the lowest Stark component in the $^3H_4$ manifold, and that (2) the ir absorption intensity is very weak there. The last observation corresponds to a low transition probability to or from the $^3H_6$ ground multiplet. This is in harmony with the observed extremely long lifetime of the energy level in question.

We have found a value of 140±10 ms for that lifetime. The same lifetime within experimental error was determined also using the absorption peak at 57 748 cm^{-1}, that at 57 293 cm^{-1}, and using the absorption between them [see Fig. 3(b)]. This indicated that in all of these we are dealing with a common initial state as depicted in Fig. 5. This unusually long lifetime, we believe, comes about through a series of resonance energy transfers among members of clusters. Previous workers[5] have determined the fluorescent lifetime at 100 K of the $^3H_4 \rightarrow {}^3H_6$ transition of Tm^{3+} in a mixed Er^{3+}-Tm^{3+} doped CaF_2 host. The Tm^{3+} concentration was 0.5% and the lifetime value stated is 11.5 ms. It is not known whether clustering was present in their samples.

Our experimental approach enabled us to isolate a single absorption of the many coexisting due to different sites in the lattice. Using this method one is to choose chopping periods such that $T \gtrsim \tau$. In passing we also observe that our ir light source and optical components guaranteed that initial excitation of the Tm^{3+} ions is limited to the $^3H_4$ and $^3H_5$ manifolds (centered at about 6000 and 8500 cm^{-1}, respectively).

In determining the spectral position of the component level of the $^3H_4$ from which our absorption proceeds to the $5d$ configuration, we have assumed that the final $4f^{11}5d$ state is identical for both spectra in Figs. 3(a) and 3(b). This is in harmony with the previously[6] made conjecture that at the upper end of the lanthanide series (Yb^{3+} and Tm^{3+}) a contraction of the $4f^{11\text{-}1}5d$ configuration is possible. Thus low-lying levels may not be affected much by the host crystal environment. It is worth noting that a curve such as that presented in Fig. 3(a) could not be obtained for the crystal used in producing the data in Fig. 3(b). It exhibited an extreme degree of opacity in the photon energy region of 63 000 cm^{-1}.

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*Permanent address: Institute of Physics, Nicholas Copernicus University, Torun, Poland.

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